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## 14. ABSTRACT

This project used two strategies to develop barrier coatings 10,000 times less permeable than those currently in existence. The first strategy used aligned impermeable flakes which reduced by roughly a factor of 50 both the permeability and the lag, that is the time before any significant penetration. The second strategy, sacrificial reagents, did not effect the permeability in the steady state limit but increased the lag by a factor of 1000 or more. The two strategies together can meet the original goal.

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**Contract/Grant Title:** Reactive Nanoengineered Coatings

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**Accomplishments:**

This project used two strategies to develop barrier coatings 10,000 times less permeable than those currently in existence. The first strategy used aligned impermeable flakes which reduced by roughly a factor of 50 both the permeability and the lag, that is the time before any significant penetration. The second strategy, sacrificial reagents, did not effect the permeability in the steady state limit but increased the lag by a factor of 1000 or more. The two strategies together can meet the original goal.

This report is more concerned with the use of unexpended funds after the bulk of the work was complete. Part of our barrier work used block copolymers to make self-assembled aligned flakes. Thus we could spray on a single polymer and have it arrange into less permeable glassy flakes to reduce the permeability. At the same time, the flexibility of the composite could remain high. In other words, we made a composite of small, crystalline, polymer flakes within a soft rubber. We made materials that had a lower permeability but a high flexibility.



This use of block copolymers led us to consider making other structures. We were especially interested with using similar polymers to make monodisperse pores in a thin polymer sheet because we recognized that these could be used as a form of water purification. While our new membranes would not remove salt from seawater, they would remove viruses and other contaminants from drinking water at rates up to 1000 times those currently practiced.

We have now succeeded in making this type of film. We have not yet showed that it has the properties expected, but we should to reach that goal within the next few months. Remember, however, that this is a small effort, a leftover from the main grant which has been completed.

#### **Archival publications (published) during reporting period:**

- White, J.D., and E.L. Cussler, "Anisotropic Transport in Flake-Filled Barrier Membranes," *J. Memb. Sci.* **278**, 225-231 (2006)
- Shimotori, T., E.L. Cussler and W.A. Arnold, "High Density Polyethylene Membrane Containing Fe<sup>0</sup> as a Containment Barrier," *J. Environ. Engng* **102**, 803-809 (2006).
- Shimotori, T., W.A. Arnold, and E.L. Cussler, "Fate of Mobile Products Generated Within Reactive Membranes," *J. Memb. Sci.* **291** 111-119 (2007).
- Cooney, D.T., M.A. Hillmyer, E.L. Cussler, and G.D. Moggridge, "Diffusion in nanoporous materials made from block copolymers," *Crystallography Reviews* **121**, 13-24 (2006).
- Phillip, W.A., J. Rzaev, M.A. Hillmyer, and E.L. Cussler, "Diffusion Through Nanoporous Block Copolymer Membranes," *J. Memb. Sci.* **286** 144-152 (2006).
- Liu, Q., E.L. Cussler, "Barrier Membranes Made with Lithographically Printed Flakes," *J. Memb. Sci.* **285** (56-57 (2006).
- Wang, J., J.P. DeRocher, L. Wu, F.S. Bates, and E.L. Cussler, "Barrier films made with various lamellar block copolymers," *J. Memb. Sci.* **270**, 13-21 (2006).

#### **ANNUAL PROGRESS SUMMARY**

### Completing the Original Objective

This research developed a scientific basis for reducing the permeability of thin films like paints and packaging by as much as 10,000 times. The research used two strategies. First it added thin, impermeable flakes to an existing film. Such flakes reduced the permeability by forcing any solutes to take a tortuous path across the film. Second, the research added reactive scavengers to the coating. These scavengers can consume any diffusing solute before it crosses the film.

Explaining how these effects are achieved is easiest in terms of a small volume immersed in a large bath of solutes and protected by a thin membrane. We will measure the concentration within this small volume as a function of time. Initially the solute concentration in that volume is zero. As time proceeds, it becomes finite after some specific lag. The concentration within the small volume then rises roughly linearly at a rate proportional to the steady state permeability of the film. Any barrier film can be characterized by these two quantities: the lag before significant penetration occurs, and the leak rate once penetration does occur.

The lag time in these films is affected both by aligned flakes and by sacrificial reagents, but it is affected more by the latter. These sacrificial reagents consume any diffusing solute and delay its penetration across the membrane. They do not, however, change the leak rate across the membrane. After all, when the solutes are exhausted, diffusion occurs just as it would in any other steady state situation.

These results are exemplified by studies of the diffusion of chlorinated hydrocarbons across polyethylene films. The polyethylene is what is actually used as a barrier for landfills. When nanoparticles of zero valent iron are blended into this membrane, they increase the lag for

chlorinated hydrocarbons by 300. The fate of products of the reactions of any reaction products can also be successfully predicted. We view these studies as essentially complete.

The other method used to improve barrier properties is that of aligned flakes. In our original work, we primarily used flakes of mica and clay. We showed that when these flakes were properly aligned, the change in permeability went with the square of the flake concentration and with the square of the flake shape. These results, now been verified by others, can serve as the basis for a large number of estimates of barrier properties, including the barrier properties of skin.

As part of our studies of flake-filled membranes, we also made membranes of block copolymers which would self-align to give flake-like structures. When one of the polymer blocks was a glass, the membrane was relatively impermeable; when the other was a rubber, it remained flexible. Thus we made composites which had flexibility dominated by the rubber and permeability dominated by the glass. Because we showed that these films were characterized by a lag time and a leak rate, we had a second new method of making barrier films.

### Extending Our Research

The work with block copolymers suggested that we could use other self-assembled film geometries to get have very significant advantages. We were especially intrigued by the idea of making a film with small pores for purifying water. We anticipate that water supplies are a major crisis looming behind concerns about energy and global warming. They are certainly a significant problem under battlefield conditions.



We tried to make pores with block copolymers in three distinct ways: by aligning the pores with shear fields, by making porous isotropic gyroid structures, and by aligning the pores using fast drying. Each is described in the following paragraphs.

#### Aligning the Pores with Shear

The first method we used completely impractical at large scale, gave us a means of seeing if these polymer, would provide the porous structure which we seek. We began with a diblock copolymer of styrene and lactic acid. We chose a concentration of lactic acid which would give the desired cylindrical phases within the polymer. We aligned these cylinders by forcing the polymer through a small orifice. We cut off pieces of the polymer and installed them in a larger membrane, just the way one would cut off pieces of pepperoni to install on a pizza. Thus we got cylindrical lactic acid regions oriented perpendicularly to the membrane surfaces. We then etched these films with base to remove the lactic acid, and we showed that these polymer structures did in fact have pores that showed promise for ultrafiltration, as shown in Figure 1(b).

The difficulty with this technique is that it is completely impractical in practice. We succeeded in making only square millimeters of membrane area, and we need square meters. Moreover, the membranes were thick, as much as 500  $\mu\text{m}$ . Thus while these experiments were useful as a proof of principle, they had no long-term value.

#### Gyroid Structures

We then switched to making a membrane based on a gyroid structure in a triblock copolymer, in which both polystyrene and the polylactic acid form a continuous phase. Such a structure can be thought of as analogous to a basket of apples. If you were a worm in that basket,

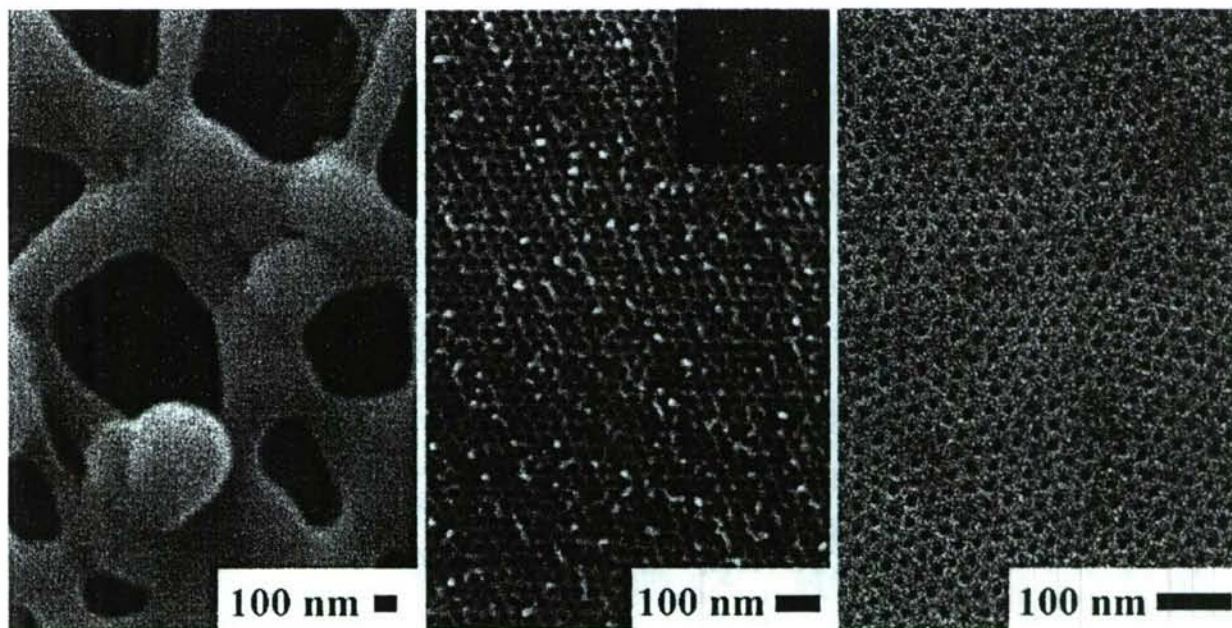


Figure 1. Three Membranes with the Same Nominal Pore Size. The membrane on the left is commercially available. That in the center is made by aligning poly(lactide) cylinders in a polymer melt with shear, then slicing off small circles, and finally etching with base. That on the right is made by casting a thin film on a solid support, quickly drying the film, and etching with base.

you could go from one side of the basket to the other staying completely within apples; the apples make a continuous phase. If you were a fly, you could also fly from one side of the basket to the other staying completely in the air. The air is also a continuous phase.

In the same way, the gyroid structure allows us to make a polymer with both a continuous lactic acid phase and a continuous polystyrene phase. This polymer was made into a thin film and then etched to open monodisperse pores. This membrane showed transport properties that made it attractive for ultrafiltration. The gyroid did not require alignment like our earlier



membranes because it is an isotropic material. Thus it circumvented the major issue of our earlier, clumsy, sheer-aligned membranes.

However, because the pores in the gyroid membranes do not have a fixed diameter but are shaped like funnels standing tip to tip, we expect that they would be difficult to use for ultrafiltration. Moreover, making polymers that actually showed the gyroid structure turned out to be much more straightforward in theoretical calculations than in the laboratory. While we did succeed, we decided that this too was not a practical goal.

### Cylindrical Pores Perpendicular to the Surface

Our current efforts center on casting films of diblock copolymers which are known to form cylindrical structures. We and others have discovered that if these films are cast rapidly from good but highly volatile solvents, they can under some circumstances form cylinders oriented perpendicularly to the surface. While no one is sure why this occurs, it probably is the result of spinodal decomposition forming small lactic acid spheres which then nucleate at the surface to reform as cylinders: on thermodynamic grounds, these cylinders would prefer to be oriented in the plane of the membrane rather than perpendicular to the membrane surface. Indeed, if we take a film with cylinders oriented perpendicular to the membrane surface and incubate it and anneal it in the presence of high concentrations of solvent vapor, the cylinders which we have trapped perpendicular to the membrane surface will reorient parallel to the membrane surface.

We have avoided this sort of annealing in the presence of solvent and instead have etched out the lactic acid to produce perpendicular pores. These pores show flow characteristics that



correspond to a diameter of 9 nm. They show the same size in electron micrographs, as shown in Figure 1(c). They have enormous promise as a means of purifying water.

#### Future Work

We want to extend these early experiments to other systems so that we can choose different polymers and different solvents for making these superior ultrafiltration membranes. We also want to show that they do in fact show the ultrafiltration properties which we expect. Although our grant with the Air Force has expired, we hope to complete these experiments over the next year. While we will not have any formal reporting responsibility for you, we still hope to be able to send you word of our success.